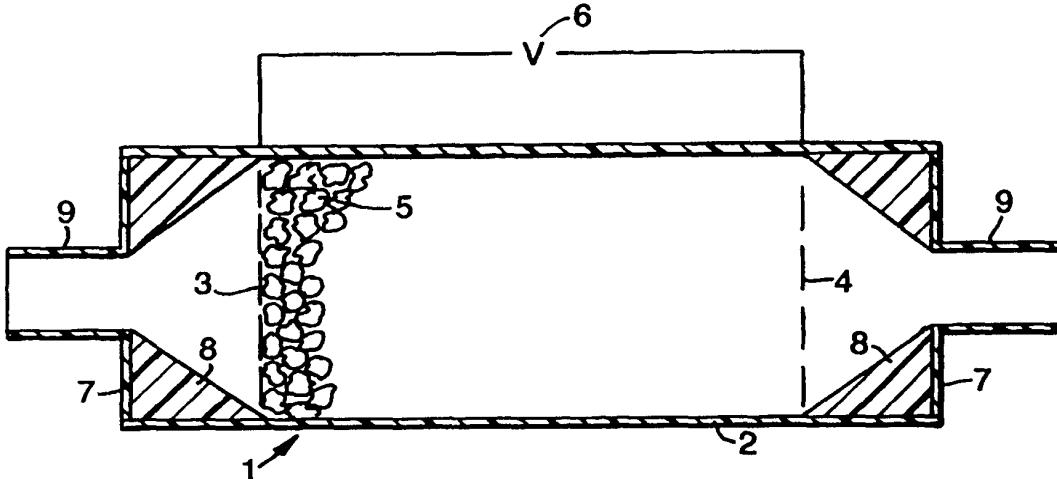


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(54) Title: TREATMENT OF GASEOUS EMISSIONS



(57) Abstract

A reactor chamber (2) forms part of an exhaust system of an internal combustion engine. Within the chamber (2) are electrodes (3 and 4) between which there is disposed a bed of active material (5) through which, in use, the exhaust gases pass. In the presence of an electrical discharge, driven by an electrical voltage applied across the electrodes (3 and 4), the active material (5) has a catalytic action in the reduction of nitrogenous oxides in the exhaust and also acts to remove hydrocarbons from the exhaust gases.

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Treatment of gaseous emissions

The present invention relates to the treatment of gaseous emissions and in particular to the reduction of 5 the emission of nitrogenous oxides (HCs for Gasoline) from the exhausts of internal combustion engines.

One of the major problems associated with the development and use of internal combustion engines is the 10 noxious exhaust emissions from such engines. Two of the most deleterious materials, particularly in the case of diesel engines, are particulate matter (primarily carbon) and oxides of nitrogen (NO_x). Excessive levels of NO_x also are produced by spark-ignition engines operating in 15 what is known as 'lean burn' mode in which the air/fuel ratio is higher than that required for stoichiometric combustion. Increasingly severe emission control regulations are forcing internal combustion engine and vehicle manufacturers to find more efficient ways of 20 removing these materials in particular from internal combustion engine exhaust emissions. Unfortunately, in practice, it is found that techniques which improve the situation in relation to one of the above components of 25 internal combustion engine exhaust emissions tend to worsen the situation in relation to the other. Even so, a variety of systems for trapping particulate emissions from internal combustion engine exhausts have been investigated, particularly in relation to making such particulate emission traps capable of being regenerated 30 when they have become saturated with particulate material.

Examples of such diesel exhaust particulate filters are to be found in European patent application EP 0 010 35 384; US patents 4,505,107; 4,485,622; 4,427,418; and

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4,276,066; EP 0 244 061; EP 0 112 634 and EP 0 132 166.

In all the above cases, the particulate matter is removed from diesel exhaust gases by a simple, physical 5 trapping of particulate matter in the interstices of a porous, usually ceramic, filter body, which is then regenerated by heating the filter body to a temperature at which the trapped diesel exhaust particulates are burnt off. In most cases the filter body is monolithic, 10 although EP 0 010 384 does mention the use of ceramic beads, wire meshes or metal screens as well. US patent 4,427,418 discloses the use of ceramic coated wire or ceramic fibres.

15 In a broader context, the precipitation of charged particulate matter by electrostatic forces also is known. However, in this case, precipitation usually takes place upon large planar electrodes or metal screens.

20 GB patent 2,274,412 discloses a method and apparatus for removing particulate and other pollutants from internal combustion engine exhaust gases, in which the exhaust gases are passed through a bed of charged pellets of material, preferably ferroelectric, having high 25 dielectric constant. In addition to removing particulates by oxidation, especially electric discharge assisted oxidation, there is disclosed the reduction of NO_x gases to nitrogen, by the use of pellets adapted to catalyse the NO_x reduction.

30 Also, US patents 3 983 021, 5 147 516 and 5 284 556 disclose the catalytic reduction of nitrogen oxides. However, US 3 983 021 is solely concerned with the reduction of NO to N in a silent glow discharge, the 35 temperature of which is kept below a value of at which

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the oxidation of N or NO to higher oxides of nitrogen does not occur. There is no mention of any simultaneous removal of hydrocarbons.

5 Although, so-called contact bodies are used in the process of US 3 983 021, and some of those disclosed may have some catalytic properties, catalysis does not appear to be a necessary feature of the process of US 3 983 021. Other surface properties, such as adsorption on large 10 surface area materials, are the basis of the process of US 3 983 021.

US patent 5 147 516 does refer to the use of catalysts to remove NO_x , but the catalytic materials 15 involved are defined very specifically as being sulphur tolerant and deriving their catalytic activity from their form rather than their surface properties.

Also, the operating conditions are very tightly 20 defined. There is no specific mention of the type, if any, of electric discharge involved. All that is disclosed is that the NO_x removal depends upon electron-molecule interactions, facilitated by the structure of the 'corona-catalytic' materials, not the inter-molecular 25 interactions involved in the present invention. There is no mention of the simultaneous removal of hydrocarbons from the gas streams being treated by the invention of US 5 147 516.

30 US patent 5 284 556 does disclose the removal of hydrocarbons from internal combustion engine exhaust emissions. However, the process involved is purely one of dissociation in an electrical discharge of the so-called 'silent' type, that is to say, a discharge which 35 occurs between two electrodes at least one of which is

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insulated. The device described is an open discharge chamber, not a packed bed device. Mention is made of the possible deposition of a NO_x -reducing catalyst on one of the electrodes.

5

US patent 5,609,736 discloses a pellet bed reactor in which the pellets of the reactor bed either incorporate a catalyst or are mixed with separate (smaller) pellets of a material which is catalytic for 10 the disruption of volatile organic compounds. The catalysts also are chosen with a view to reduce the production of carbon monoxide as a by-product of the disruption of the volatile organic compounds. The only volatile organic compound dealt with in the text of the 15 specification is carbon tetrachloride. Nowhere in US patent 5,609,736 is there any method demonstrated for the treatment of nitrogen or its compounds.

US patent 5,149,511 discloses a system for reducing 20 NO_x emissions from oxygen-rich internal combustion engine exhaust gases in which partially oxygenated light organic compounds such as alcohols, aldehydes, ketones and ethers, are injected into the exhaust gases which are then passed over a bed of a copper-containing ZSM5 25 zeolite and then a bed of an oxidising catalyst such as Pt doped alumina or 1% Pd/10% $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$.

Although the partially oxygenated organic compound is described as a reductant, presumably in combination 30 with the zeolite catalyst, no information is given as to the chemistry involved, neither is there given any explanation of the role of the oxidation catalyst, nor as to why it should be downstream of the reducing stage. Furthermore, no plasma enhancement is involved, the only 35 energy input seems to be the thermal energy of the

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exhaust gases.

US 5,711,147, published after the priority date of this application, discloses a plasma-assisted catalytic 5 reactor to reduce the emission by internal combustion engines of NO_x and, possibly, carbonaceous particulates. The system is for use with oxygen-rich exhaust gases from diesel and lean-burn spark ignition engines.

10 In the system described a hydrocarbon such as diesel fuel is cracked into simpler hydrocarbons by a corona discharge and mixed with oxygen-rich exhaust gases from which NO_x is to be removed. The mixed hydrocarbons and exhaust gases are then passed through another region of 15 corona discharge, which may include silica beads as a particulate trap. In this region, NO_x is oxidised to NO_2 . The NO_2 plus excess hydrocarbons are passed through a bed of a catalyst which acts to reduce the NO_2 to O_2 and N_2 and to oxidise the hydrocarbons to CO_2 and H_2O . No plasma 20 is involved. The effluent from the catalyst bed is passed through a second bed of an oxidising catalyst which oxidises remaining hydrocarbons to CO_2 and H_2O .

The use of corona discharges as the plasma source 25 has the disadvantage that such discharges can only be successfully established over limited distances between the discharge electrodes, so that the dimensions of the plasma processing regions, and hence the throughput of exhaust gas, correspondingly is limited. Pulsed corona 30 sources can be used to overcome some of the disadvantages but when reduced to practice they are inhibited by the cost, complexity, durability and electromagnetic emissions associated with short pulse, high voltage power

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supplies. The actual NO_2 reduction and hydrocarbon oxidation take place without the assistance of plasmas.

US patent 5,715,677, published after the priority 5 date of this application discloses a system for reducing NO_x and particulate emissions from diesel exhausts using plasma-regenerated absorbent beds.

Two beds are used, one of which absorbs NO_x and 10 particulates and the other of which reduces NO_x and oxidises carbonaceous particulates using a plasma in combination with the catalytic properties of the absorber beds. The beds are used alternately.

15 However, the plasma seems to be used solely to heat the catalyst bed to a temperature in the range 300 - 900°C and plays no part in the actual decomposition of the NO_x and oxidation of carbonaceous particulates.

20 PCT application WO98/09699, published after the priority date of this application, incorporates the subject matter of the application which resulted in US patent 5,711,147. It discloses a further arrangement in which oxygen-rich exhaust gases are passed through a bed 25 of an oxidising catalyst such as platinum-doped alumina in which NO_x in the exhaust gases is oxidised to NO_2 , hydrocarbons are mixed with the effluent from the oxidiser and the mixture is passed through a bed of a reducing catalyst such as γ -alumina in which the NO_2 and 30 hydrocarbons are reduced to N_2 , CO_2 and H_2O .

No plasma enhancement of the actions of the catalysts is involved in this arrangement.

A paper 'Selective Catalytic Reduction of NO_x with N-Free Reductants' by M. Shelef published in Chem Rev 1995 pp 209 - 225 is a comprehensive review of the use of 5 zeolites in particular, in association with hydrocarbons for the reduction of the NO_x content of internal combustion engine exhaust gases. Other catalysts are mentioned but not dealt with comprehensively. The paper is concerned solely with non-plasma assisted catalysis 10 and is academic in nature, disclosing no practical systems.

While many candidate materials and compositions have been suggested for lean NO_x catalysis in internal 15 combustion engine vehicle applications, the zeolite family of materials are considered to offer the best opportunity for development of a commercial system. Synthetic zeolites are usually crystalline aluminosilicate materials with large surface area and 20 channel structures with a well defined porosity. Several mechanisms have been proposed for the activity of the zeolites but at this time it is not clear that any single mechanism is responsible. Mechanisms believed to be operative include, but are not limited to; NO 25 decomposition, partially oxidised hydrocarbon reactions with NO, formation and decomposition of organonitrogen species and bifunctional reactions involving activated hydrocarbons with NO_2 . Further detailed analysis suggests possible roles of free radicals in these processes. The 30 relative importance of different mechanisms appear to vary with many factors, including but not limited to; the zeolite, the exchanged metal or metals, the exchange level, the temperature and the composition of the gas containing the NO_x to be reduced. While the exact

mechanism may not be understood in detail for a given system it is the structure and surface activity of the zeolites which allow them to catalyse the lean NO_x reactions.

5

One of the most significant factors limiting the commercial use of zeolites in lean NO_x internal combustion engine vehicle catalysts has been their limited hydrothermal stability. The zeolites lose performance and 10 irreversibly degrade at temperatures that would be required in most vehicle applications. The mechanisms for the loss of stability are again not completely clear and depend on the exchanged metal in the zeolite. Studies suggest that Cu doped ZSM-5, one of the more active 15 zeolites degrades at higher temperatures by sintering and or decomposition and dealumination of the crystal lattice.

Recently it has been shown that introducing iron 20 into the zeolite structure significantly increases the hydrothermal stability of the material. While understanding of the mechanisms for the promoted stability are not definitive it has been suggested that it is linked to the removal of certain catalytically 25 active sites on the zeolite, in particular the Bronsted acid sites.

In order to be of practical use in a vehicle catalyst application the hydrothermally stabilised 30 zeolite must have a high activity and selectivity for reduction of NO_x to N₂ as this results in a high space velocity and low package size for the catalyst.

A non-thermal plasma, such as is described in GB 35 patent 2,274,412 and more particularly as described

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herein, can be engineered to produce many of the active species that are implicated in lean NO_x catalysis over zeolites and described previously. In particular hydrocarbons can be activated as well as partially 5 oxygenated and NO can be converted to NO₂, all functions that have been proposed to occur on zeolite active sites and hence potentially inhibited in hydrothermally stabilised zeolites.

10 Based on these observations and current understanding of the structure of hydrothermally stable zeolites, in particular the corresponding removal of catalytically active sites, it is an appreciation upon which the present invention is based that the synergistic 15 interaction of a plasma and a catalyst is key to the realisation of a commercially viable lean NO_x aftertreatment system for internal combustion engine vehicle applications.

20 It is an object of the present invention to provide an improved method for the removal of carbonaceous particulates and nitrogenous oxides from the exhaust gases emitted by internal combustion engines.

25 According to the present invention there is provided a method of treating gaseous media including nitrogenous oxides, characterised in that there is included the operation of passing a gaseous hydrocarbon through a reactor system including a bed of a gas permeable plasma 30 enhanced oxidative first material comprising a dielectric material having oxidative properties in the presence of a non-thermal plasma, applying a potential across the reactor bed sufficient to establish a plasma in the hydrocarbons in the interstices in the reactor bed 35 material thereby to produce plasma activated hydrocarbon

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and contacting a combination of the plasma activated hydrocarbon and the gaseous medium with a second material adapted in the presence of the plasma activated hydrocarbon to catalyse the reduction of the nitrogenous 5 oxides to nitrogen.

By plasma activated hydrocarbon we mean hydrocarbon the activity of which has been enhanced in a plasma by for example partial oxidation, free radical formation, 10 ionisation and/or energy absorption (eg. into vibrational or rotational modes).

Also according to the present invention there is provided a reactor system for treating gaseous media, 15 including a reactor chamber including at least two electrodes between which there is a gas permeable reactor bed, and means for constraining the gaseous emissions to pass through the reactor bed, characterised in that the reactor bed includes a first material adapted to 20 facilitate the establishment of an electric discharge in the interstices of the material of the reactor bed and to have oxidative properties in the presence of a plasma, and a second material adapted in the presence of plasma activated hydrocarbon to have a catalytic action in the 25 reduction of any nitrogenous oxides included in the gaseous medium passing through the reactor bed.

Also according to the invention there is provided a reactor system for the treatment of a gaseous medium 30 including nitrogenous oxides, characterised in that there is provided a source of a gaseous hydrocarbon, a reactor to which the source of the gaseous hydrocarbon is connected, the reactor containing a gas permeable bed of a material adapted to have oxidative properties in the 35 presence of a plasma, a second reactor including a material adapted in the presence of plasma activated

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hydrocarbons to catalyse the reduction of nitrogenous oxides to nitrogen, and means for combining plasma activated hydrocarbons from the reactor with the gaseous medium prior to the combination passing into the reactor.

5

Examples of suitable active materials for the reactors are the aluminas known as Alcoa LD-350, Catal Industrial CT-530, Condea Hollow Extrudates, DYPAC, T-60 Alumina, Cordierite, α , χ and γ Aluminas and Aluminas containing mixtures of these phases (including tabular, fused and activated aluminas) Cu-doped DYPAC, glass beads, Fecralloy, Silica Gels and other water absorbing materials, P2 graded foams, and Puremet foams, ferroelectric, dielectrics, ceramics, silicas, polymers.

10 These materials may be coated with various washcoats including zeolites, V_2O_5 , V_2O_5/Pt coats and a coating derived from an aqueous dispersion of flame hydrolysed alumina powder. There is also scope for the use of current state of the art automotive catalysts in

15 monolithic, pelletised and foam forms. Preferred materials for the active element are zeolites, in particular, zeolites containing iron, cobalt or copper with or without additional catalyst promoting cations such as cerium and lanthanum.

20

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Materials with a photocatalytic effect such as titanium dioxide some or all of which is in the anatase form; or cerium dioxide are suitable as they are activated by the ultra-violet light generated in the

30 electrical discharge.

The form of the active material is desirably such as to provide high exposed surface area for maximising available reaction sites per unit volume for gas passing through the reactor. The active material may have open

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porosity such that it is itself permeable to gas.

These materials may be of use in the following forms or as washcoats applied to the following forms : beads, 5 foams, honeycomb monoliths, extrudates of single or mixed oxides, wires, wire wools, weaves, bobbins, bonded or pressed sheets, discs and rolls. The honeycombs may be used in a variety of different geometries including a cordierite one in which its channels are alternately open 10 and closed so that the combustion exhaust gas passes through the porous walls of the honeycomb. For ease of production and durability, aluminium metal may be used, provided, by anodising, with an alumina surface layer.

15 The reactor bed may be made of a mixture of materials, one of which has a high dielectric constant, and preferably is ferroelectric, and the other of which, while also dielectric is chosen for its catalytic activity with respect to the reduction of oxides of 20 nitrogen.

In one arrangement the reactor chamber has two sections in one of which there are pellets of a ferroelectric material having a high dielectric constant 25 and in the other of which there is the active material adapted to catalyse the reduction of nitrogenous oxides in the exhaust gases to nitrogen, the arrangement being such that the exhaust gases pass through the pellets of ferroelectric material before the active material.

30

The invention will now be described, by way of example, with reference to the accompanying drawings, in which

35 Figure 1 shows, schematically, a cross-section of an embodiment of the invention, in which exhaust gases from

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an internal combustion engine are arranged to flow axially through a bed of catalytically active gas permeable material;

5 Figure 2 (a) to (c) show, schematically, different arrangements of catalytically active material embodying the invention;

10 Figure 3 shows, schematically, a second embodiment of the invention;

15 Figure 4 shows schematically a third embodiment of the invention in which the exhaust gases are arranged to flow radially through a bed of catalytically active material,

Figure 5 shows schematically a second form of radial flow reactor embodying the invention,

20 Figure 6 shows how the concentration of carbon monoxide and NO_x in the effluent from a reactor embodying the invention and having a reactor bed including a mixture of pellets of barium titanate and zirconia varies with the percentage of zirconia in the mixture, and

25 Figure 7 shows how the concentration of carbon monoxide and NO_x in the effluent from a reactor embodying the invention and having a reactor bed including a mixture of pellets of barium titanate and titania varies with the percentage of titania in the mixture.

30 Figures 8a, 8b and 8c show conceptual flow diagrams of embodiments of the invention in which additional hydrocarbons are added to exhaust gases from internal combustion engines.

Referring to Figure 1, a plasma reactor 1 for particulate and other combustion products and simultaneously controlling or removing NO_x from the 5 exhaust of an internal combustion engine consists of a chamber 2 made of an insulating refractory material, in which there are two metallic grids 3 and 4, respectively. Between the grids 3 and 4 there is a loosely packed reactor bed 5 of a particulate reactor material which, in 10 the presence of an electric field which is sufficient to establish a plasma in an internal combustion engine exhaust gas flowing through the reactor bed 5 of the reactor 1, is capable of causing the reduction of nitrogen oxides in the exhaust gas to nitrogen. The 15 grids 3 and 4 are connected to an AC power supply 6 capable of charging the particulate material in the reactor bed 5 to a potential sufficient to excite the exhaust gases to a plasma state. Between each of the grids 3 and 4 and the adjacent end walls 7 of the reactor 20 chamber 2 are conical gas flow smoothers 8. Again, these are made of an insulating material. Stubs 9 forming part of the end walls 7 of the reactor chamber 1 enable it to be coupled into an exhaust system of an internal combustion engine, neither of which is shown in the 25 Figure 1.

Suitable materials for the reactor bed 5 of particulate material are beads of γ -alumina, and/or silica either as such or doped with alkali metals, alkaline 30 earths or metals with catalytic properties such as the transition and noble metals. Zeolites also can be used, particularly if they contain iron, copper or cobalt with or without additional catalyst promoting cations such as cerium and lanthanum. Pellets of the alumina/silica 35 based materials and zeolites are effective in bead form.

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Zeolite pellets are also effective in the form of short tubes.

Suitable potentials are of the order of tens of 5 kilovolts.

In use, the high potential applied across the electrodes 4 and 3 is such as to excite a non-thermal plasma in the exhaust gases in the interstices between 10 the pellets 5. A convenient potential for this purpose is a potential of about 10 kV to 30 kV which may be regularly pulsed direct potential or a continuously varying alternating potential, or may be an interrupted continuous direct potential.

15

Anatase phase titania is suitable for the removal of particulate carbon and nitrogenous oxides from diesel and other internal combustion engine exhaust gases because anatase titania has photocatalytic properties in the 20 presence of ultraviolet radiation, and such radiation is generated by the plasma discharges within the interstices of the reactor beds of reactors such as those described. The ultraviolet radiation excites electrons from the valence to the conduction band of the titanium atom. 25 This excitation results in the formation of holes at the positions in the crystal lattice of the titanium atoms and free electrons. The free electrons cause reduction reactions to occur and the holes cause oxidation reactions to occur, both of which facilitate the removal 30 of carbonaceous and nitrogenous combustion products from internal combustion engine exhaust gases.

Particularly suitable for use for the above purpose are anatase phase titania pellets manufactured by the 35 Norton Chemical Process Products Corporation and marketed under their product code number XT 25376. These pellets

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contain 99% by weight titania and 0.1% by weight of SO_4 . These pellets have a nominal surface area of $139 \text{ m}^2 \text{ g}^{-1}$, a median pore diameter of 16 nm, a total pore volume of $0.38 \text{ cm}^3 \text{ g}^{-1}$, and a density of 0.836 g cm^{-3} . This material 5 has the property that it does not adsorb water from the vapour phase, which is advantageous in connection with the treatment of internal combustion engine exhaust gases.

10 In the structured rutile phase, the permittivity ϵ of titania is anisotropic, and higher than the permittivity of isotropic titania phases (i.e. phases which do not contain structured rutile phase). This isotropic titania has a permittivity of the order of 15 whereas for 15 structured rutile phases quoted values are $\epsilon_{11} = 86$, $\epsilon^{22} = 86$ and $\epsilon_{33} = 170$ for measurement at 300 K and $10^4 - 10^6 \text{ Hz}$. High permittivity is beneficial for generating a non-thermal plasma, so if structured rutile phase is present improved performance can be anticipated.

20 Zirconia in some forms also has catalytic properties for the reduction of nitrogenous oxides. One such form of zirconia is that manufactured by Norton Chemical Process Products Corporation and marketed under their 25 product code XZ 16052. In pellet form this material has a nominal surface area of $95 \text{ m}^2 \text{ g}^{-1}$, a pore volume of $0.31 \text{ cm}^3 \text{ g}^{-1}$ and a density of 1.17 g cm^{-3} . This form of zirconia has the property that it does not adsorb water from the vapour phase. It also has a bimodal pore structure with 30 the respective pore diameters centred around 40 nm and 8 nm.

Further, when pellets of zirconia in this form are

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mixed in the gas permeable reactor bed with pellets of anatase titania there is a symbiotic improvement in performance in the treatment of internal combustion engine exhaust gases as compared with the performance of 5 the zirconia or anatase titania on their own. It is convenient for this purpose to provide equal parts by volume of titania and zirconia in the mixture.

10 The gas permeable reactor bed is not restricted to a single substrate packing or shape. The material of the reactor bed may be in the form of a graded pelletised bed or graded porosity foam. For example the inlet side to the foam could have a relatively large pore size which decreases through the length of the bed, as shown in 15 Figure 2(a). This helps to reduce asymmetric soot deposition in the bed as the soot penetrates deeper and more uniformly into the substrate reducing the possibility of degrading the uniformity of the electric field distribution between the electrodes.

20 The gas permeable bed may have a mixed structure, for example, a foam section 21, followed by a honeycomb section 22, as shown in Figure 2(b), preferably arranged so that incoming exhaust gases impinge on the foam region 25 21, which has the effect of dispersing the exhaust flow. The foam region 21 of the bed then acts as both an emissions reducer and a flow distributor, sending the gas evenly through the honeycomb section 22.

30 Significant water absorption with some of the bed materials has been observed for the bed of active material and this must be taken into account in the selection criteria. One solution may be to bleed air into the gas stream which could dilute the exhaust gas 35 and may then help prevent sooting up and water absorption.

Alternatively, one can have a mixed bed which consists of layers of silica gel 23 (or activated carbon or any suitable material with capability of drying the 5 gas) upstream of the active material as shown in Figure 2(c). If the exhaust is flowed through the drying bed, first, on cold start the water is removed from the exhaust gas allowing the active material to treat dry gas. As the exhaust heats up a thermal switch (not 10 shown) cuts in, redirecting the flow across the active material only, where NO_x particulate material reduction takes place. The heat of the exhaust gas can be used to recondition the water absorbing bed, so that when the temperature drops or water becomes a problem, exhaust gas 15 flow can be switched back initially through the silica gel layers 23. Condensate forming after use and cooling of the converter would be absorbed by the silica gel 23 or activated carbon, which is then reconditioned as the exhaust gas warms up the bed of active material, on the 20 next use of the internal combustion engine to which the reactor is fitted.

The reactor bed 5, as shown in Figure 1, may include also, pellets of high dielectric constant active 25 materials such as those described in our earlier patent GB 2,274,412 which are effective for the removal of carbonaceous contaminants from internal combustion engine exhaust gases. A preferred material for this purpose is barium titanate. Calcium titanate is a suitable 30 alternative.

If these materials are used, then although they can be mixed with the nitrogenous oxide reducing material, it is possible for the two to be kept separate, with the 35 high dielectric constant material pellets being upstream

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of the other material, as shown in Figure 3, in which those components which are common to both embodiments of the invention have the same reference numerals.

5 Referring to Figure 3, a body 31 of pellets of a high dielectric constant ceramic material such as barium titanate, is situated upstream of the bed 5 material capable of reducing nitrogenous oxides contained in internal combustion engine exhaust gases and separated
10 from it by a metal grid 32, so as to form a combined reactor bed 33. A voltage sufficient to excite into a plasma state exhaust gases passing through the reactor is applied across the combined reactor bed 33.

15 In a variant of this system the plasma exciting voltage is applied across the pellets 31 of barium titanate only. The reaction products in the plasma from the bed of pellets 31 of barium titanate pass into the nitrogenous oxide reducing portion of the reactor bed 33
20 where they are reduced to primarily nitrogen.

Referring to Figure 4, a reactor 401 for the treatment of internal combustion engine exhaust gases to reduce emissions of pollutants such as carbonaceous and
25 nitrogenous combustion products therefrom consists of a stainless steel reactor chamber 402 which has an inlet stub 403 and an outlet stub 404, by means of which it can be connected into the exhaust system of an internal combustion engine (not shown). The chamber 402 is
30 arranged in use to be connected to an earthing point 405. Within the chamber 402 are a cylindrical inner electrode 406 made of perforated stainless steel sheet and an earthed outer electrode 414 co-axial with the inner electrode 406 and also made of perforated stainless steel
35 sheet. The electrodes 406 and 414 are held in position by two insulating supports 407 and 408. The space 411

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between the electrodes 406 and 414 and the supports 407 and 408 is filled with a reactor bed 411 of pellets illustrated highly diagrammatically at 412 made of barium titanate and titania or zirconia or a mixture as 5 discussed further below. The upstream electrode support 407 has a number of regularly spaced axially-oriented holes 413 around its periphery so that exhaust gases entering the reactor 401 pass into the space 415 between the outer electrode 414 and the wall of the chamber 402 10 before passing radially through the bed of pellets 412 and leaving the reactor 401 via the inner electrode 406, as shown in the drawing. An insulated feed-through 410 connects output from a source 409 of electrical potential to the inner electrode 406. The potential thus applied 15 across the reactor bed 411 is sufficient to excite a plasma within the interstices between the pellets 412 of the reactor bed 411. A convenient potential for this purpose is about 10 kV to 30 kV, and may be a pulsed direct or continuously varying alternating potential, or 20 may be an interrupted continuous direct potential.

Referring to Figure 5 there is shown in part section the mesh electrode assembly of a radial flow reactor chamber similar to that described in our earlier patent 25 GB 2 214 142 with reference to Figure 2.

Inner and outer mesh electrodes 501, 502, respectively terminate in ceramic end pieces 503, 504, respectively, which abut a ceramic end flange 505. The 30 end-piece 503 of the inner mesh electrode 501 has an inward flare 506 and is located in a recess 507 in the end flange 505 and the outer edge of the end-piece 504 has a flare 508. The flares 506 and 508 of the end-pieces 503, 504, respectively, increase the length of 35 possible leakage paths from the ends of the mesh electrodes 501, 502, so reducing the possibility of

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arcing from the mesh electrodes 501, 502. As with the axial-flow reactor chamber, the bed of active material can be particulate with the size of the particles being graded, made of different types of material or have a 5 drying layer of silica gel or activated carbon or other suitable water absorbing material, but in this case, the variations in the material of the bed occur in a radial sense. The other ends of the inner and outer electrodes 501, 502 are located in another ceramic flange 509, which 10 has an axial passage for the exhaust gases being treated. The flange 509 has a feed-through 510 for a high voltage power supply, not shown, to the inner electrode 501. A recess 511 in the flange 509 enables the insulation 512 15 as feed-through 510 to abut accurately the flange 509, so reducing the risk of electrical leakage.

The two-section arrangement of the reactor bed described with reference to Figure 2 also can be used in the radial-flow arrangements described with reference to 20 Figures 4 and 5, the grid 22 being replaced by a suitably disposed cylindrical grid.

In all embodiments of the invention the applied voltage can be either AC or DC, and if DC it can be in 25 pulsed form. In the case of AC or pulsed DC applied voltages, it is believed that in certain circumstances it is advantageous for the voltage rise time to be as short as is practicable.

30 Although the invention is effective with applied voltages in the range 15 to 30 kV and frequencies in the range 50 Hz to 15 KHz, higher frequencies can confer advantages, for example, frequencies of the order of tens of KHz appear to allow more efficient transfer of 35 electrical energy into the exhaust gases, and the faster rise time of the voltage peaks can yield more efficient

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energy release into the plasma.

It is an advantage if the nitrogenous oxide reducing materials used for the reactor beds subjected to an 5 electrical discharge in the various embodiments described have negative coefficients of resistance as in this case as the bed 5 heats up to its normal operating temperature the amount of power absorbed by the bed 4 of reactor material will decrease.

10

Certain materials capable of catalysing the reduction of NO_x to N_2 act also as a trap for NO_x which can be removed and reduced by periodically raising the temperature. Where such materials are used in the 15 embodiments of the present invention, it is possible to effect removal and reduction of trapped NO_x by periodic or continuous application of the electric discharge. It is thus possible to provide either a combined bed which traps both particulate matter and NO_x with periodic or 20 continuous application of appropriate electric discharge.

At least some of the electrical energy required to power the source of the plasma-generating voltages can be generated by means of thermo-electric devices arranged to 25 be exposed to the heat of the exhaust gases.

In use, particularly if beds of non-conducting active material are used, variations in the electric field gradient can occur, which may lead to localised 30 arcing within the reactor bed. This phenomenon can be reduced by inserting sheets of electrically conducting, preferably gas permeable, material at intervals throughout the active bed and allowing these intermediate electrodes to "float" in terms of electric potential. If 35 the reactor is of the axial flow type, then the

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intermediate electrodes can take the form of a number of parallel disks; if the reactor is of the radial flow type then the intermediate electrodes can take the form of a number of co-axial cylinders.

5

It is to be noted that, whether the reactor is of the axial or radial flow type, the cross-section of the reactor does not have to be circular. As with conventional silencers, the reactors can have elliptical 10 cross-sections.

As the creation of plasma is more efficient at lower pressures, steps can be taken to reduce the gas pressure within the reactor chamber compared with the remainder of 15 the exhaust system. One way of doing this is to provide an expansion chamber at the inlet end of the reactor and to increase the diameter of the outlet from the reactor chamber.

20 Laboratory results obtained using a reactor chamber as described in Figure 1 for some of the above materials are given in the following examples:

Example 1: Activated alumina beads (γ -alumina) (LD-
25 350, 4mm, Alcoa)

Material		NO _x (ppm)	NO (ppm)	NO _x (ppm)	CO (ppm)	CO ₂ (%)	THC (ppm)
	Blank/Bypass	323 \pm 2	243 \pm 2	81 \pm 4	763 \pm 10	3.69 \pm 0.02	627 \pm 145
30 LD-350	Bed Voltage 18kV	127 \pm 21	30 \pm 3	97 \pm 18	808 \pm 5	3.69 \pm 0.04	355 \pm 13

(THC = Total Hydrocarbon Content)

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Example 2: Activated alumina beads (γ -alumina)
 (CT530 4 mm, CATAL International).

Material		NO _x (ppm)	NO (ppm)	NO _x (ppm)	CO (ppm)	CO ₂ (%)	THC (ppm)
	Blank/Bypass	325±4	246±3	80±3	805±10	3.78±0.02	570±159
CT 530	Bed Voltage 18kV	91±20	23±4	68±16	877±5	3.74±0.02	270±10

Example 3: Alumina (Activated) from Condea-Chemie.

Material		NO _x (ppm)	NO (ppm)	NO _x (ppm)	CO (ppm)	CO ₂ (%)	THC (ppm)
Condea	Blank/Bypass	304±1	235±1	69±1	775±6	3.72±0.01	790±47
Hollow	Bed Voltage 18kV	99±18	34±3	65±17	787±6	3.68±0.03	423±12

Table 1, below, and Figure 6 show how, in a radial flow reactor such as that described with reference to Figure 1 and using a reactor bed consisting of a mixture of pellets of barium titanate and titania, the concentration of NO_x and carbon monoxide change for different operating voltages and barium titanate/titania mixtures.

25

Table I
 Changes in CO and NO_x as a function of titania percentage
 and voltage in a axial flow pellet bed reactor

Titania (%)	Barium Titanate (%)	Change in CO (ppm)	Change in NO _x (ppm)	Voltage (kV)
100	0	0+ 10 +10	-35 -60 -80	0 16.0 17.7

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Titania (%)	Barium Titanate (%)	Change in CO (ppm)	Change in NO _x (ppm)	Voltage (kV)
5	75	25	0	-40 0
			+10	-50 10.6
			+25	-60 12.4
			+35	-80 14.4
			+60	-110 16.0
	50	50	0	-30 0
			+10	-35 8.8
			+20	-40 10.6
			+70	-10 12.4
			+120	+30 14.1
			+140	+60 16.0
10	25	75	0	-25 0
			+70	+50 15.0
	0	100	0	0 0
			+20	+40 5.3
			+50	+70 7.1
			+100	+120 8.8
			+105	+200 10.6
			+220	+290 12.4
			+310	+350 14.1
			+350	+400 16.0

The highly oxidative effect of the barium titanate in these examples (as may be seen from the 100% barium titanate example) is the consequence of the use of a particular form and preparation of the barium titanate and the bed configuration of the apparatus used in generating these results.

It can be seen from Figure 6 that the most effective range of mixtures of barium titanate and titania both in respect of reducing NO_x and removing carbonaceous constituents of vehicle exhaust gases, is between 20 and 80 per cent of titania.

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Table II and Figure 7 show similar results for mixtures of barium titanate and zirconia. Again, a most effective range of 20% - 80% zirconia occurs, with a 50/50 mixture being optimum.

5

Table II
Changes in CO and NO_x as a function of zirconia percentage
and voltage in the pellet bed reactor

10

Zirconia (%)	Barium Titanate (%)	Change in CO (ppm)	Change in NO _x (ppm)	Voltage (kV)
15	100	0	-100	0
		+40	-150	16.0
	75	0	-140	0
		+50	-200	16.0
	50	0	-100	0
		+100	-30	14.1
		+130	0	16.0
20	25	0	-50	0
		+80	+30	14.1
	0	0	0	0
		+20	+40	5.3
		+50	+70	7.1
		+100	+120	8.8
		+150	+200	10.6
		+220	+290	12.4
		+310	+350	14.1
		+350	+400	16.0

30 Figures 8(a) to 8(c) show three embodiments of the invention in which a hydrocarbon is added to exhaust gases from an internal combustion engine. Common features have the same reference numerals.

35 Referring to Figure 8(a) a hydrocarbon, which may be the same fuel as is used in an internal combustion engine

from the exhaust gases of which nitrogenous oxides and carbonaceous particulates are to be removed, or another hydrocarbon such as propene is passed from a source 801 through a plasma activated pellet bed reactor 802, such 5 as those described with reference to Figures 1 or 4 above, and the plasma activated hydrocarbon output from the reactor 802 is injected into a duct 803 through which the exhaust gases, indicated by the arrow 804 are flowing. The mixture is then passed through, or over, a 10 bed 805 of a reducing catalyst such as the zeolite known as H-ZSM-5 or the zeolite known as mordenite, which have $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 51 and 35 respectively. The zeolites may include ions of catalytically active metals such as iron, cobalt or copper with or without additional 15 catalyst promoting cations such as cerium or lanthanum.

The catalyst bed 805 may include electrodes (not shown) so that a plasma can be created within its interstices, as in the case of the reactor 802, 20 particularly if the reducing catalyst is in the form of beads or pellets of extrudate.

The pellet bed reactor 802 at least partially activates the hydrocarbons passing through it. These 25 plasma activated hydrocarbons then react with the NO_x in the exhaust gases in the presence of the catalyst to produce N_2 and other benign products such as water.

Figure 8(b) shows a system in which the hydrocarbon 30 801 is combined with the exhaust gases 804 before passing into a two-stage reactor such as those described with reference to Figures 2, or in the unillustrated modification of the Figure 4 embodiment, in which there is a plasma activated oxidising bed (806) of BaTiO_3 ,

pellets followed by a bed (805) of reducing catalyst adapted to reduce nitrogenous oxides to nitrogen and water, as before. Again, appropriate catalysts for the bed (805) are zeolites such as those mentioned above, in 5 bead, extrudate, foam or monolithic form.

Figure 8(c) shows a system in which the arrangement of Figure 8(a) is combined with a second plasma enhanced pellet bed reactor (807) such as that described with 10 reference to Figure 1 or Figure 4, through which the exhaust gases (804) are passed before the plasma activated hydrocarbons from the reactor 802 are injected into them. As with the Figure 8(a) embodiment, the reducing catalyst may be in the form of beads, 15 extrudates, foams or monoliths of zeolites.

Although not illustrated, another version of the Figures 8(a) 8(b) and 8(c) embodiments uses a mixed bed of oxidising, plasma supporting high dielectric or 20 ferroelectric material mixed with the reducing catalyst (805). This is preferred when the catalyst bed (805) is required to sustain a plasma.

An advantage of the systems described above is that 25 the source of the hydrocarbons can be the same fuel as is used in the internal combustion engine, so that there is no need to provide separate storage and supply systems, nor the need to ensure the availability of other materials.

30

The invention is not restricted to the details of the foregoing examples. For instance, the reactor system or the method of the invention may utilise a reactor bed and power supply configuration as described in our patent 35 application PCT/GB98/02061 filed 13 July 1998.

Claims

1. A method of treating gaseous media including nitrogenous oxides, characterised in that there is included the operation of passing a gaseous hydrocarbon through a reactor system including a bed of a gas permeable plasma enhanced oxidative first material comprising a dielectric material having oxidative properties in the presence of a non-thermal plasma, applying a potential across the reactor bed sufficient to establish a plasma in the hydrocarbons in the interstices in the reactor bed material thereby to produce plasma activated hydrocarbon and contacting a combination of the plasma activated hydrocarbon and the gaseous medium with a second material adapted in the presence of the plasma activated hydrocarbon to catalyse the reduction of the nitrogenous oxides to nitrogen.
2. A method according to claim 1 characterised in that the gaseous medium includes carbonaceous particulate material and the gaseous medium also is subjected to oxidation by said first material.
3. A method according to claim 2, characterised in that the gaseous hydrocarbon is combined with the gaseous medium and both are passed through the same reactor bed of the said first material.
4. A method according to claim 3, characterised in that the said first material and the said second material are intimately associated and in that the ratio of the surface areas of the first material and second material lies in the range twenty to eighty per cent.
- 35 5. A method according to claim 3, characterised in that the reactor bed consists of a mixture of pellets of the

- 30 -

first material and the second material.

6. A method as claimed in any of claims 1 to 3, characterised in that the reactor system is divided into 5 separate regions, containing, at least predominantly, the first material or the second material.

7. A method as according to claim 6, characterised in that the gaseous medium and hydrocarbons are caused to 10 pass through the region containing the first material before the region containing the second material.

8. A method according to any preceding claim, characterised in that the first material is a 15 ferroelectric material.

9. A method according to claim 8, characterised in that the first material is barium titanate or calcium titanate.

20 10. A method according to any preceding claim, characterised in that the second material is selected from the group comprising the aluminas known as Alcoa LD-350, Cotal Industrial CT-530, Condea hollow extrudates, 25 T-60 Alumina, Codierite, α , γ and χ aluminas, mixtures of these phase aluminas; zeolites, and oxides of cerium, titanium, vanadium and zirconium.

11. A method according to any preceding claim, 30 characterised in that the second material is photocatalytic.

12. A method according to claim 11, characterised in that the second material is titanium dioxide or cerium 35 dioxide.

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13. A method according to claim 10, characterised in that the second material is titania in the anatase phase.
14. A method according to claim 10, characterised in 5 that the second material is titania in the textured rutile phase.
15. A method according to claim 10, characterised in that the second material is a mixture of anatase and 10 textured rutile titania.
16. A method according to claim 10, characterised in that the second material is zirconia.
- 15 17. A method according to claim 10, characterised in that the second material is a mixture of equal parts by volume of anatase phase titania and zirconia.
18. A method according to any preceding claim 20 characterised in that there is included the operation of removing water from the gaseous medium before passing the gaseous medium through the reactor bed.
19. A method according to any of claims 1 to 10, 25 characterised in that the second material is a zeolite.
20. A method according to claim 19, characterised in that the zeolite contains iron, or cobalt, or copper.
- 30 21. A method according to claim 20, characterised in that the zeolite further contains cerium or lanthanum as catalyst promoting cations.
23. A method according to claim 19, characterised in 35 that the zeolite is that known as HZSM-5, with or without a catalytically active metal dopant.

24. A method according to claim 19, characterised in that the zeolite is that known as mordenite, with or without a catalytically active metal dopant.

5

25. A method according to any preceding claim, characterised in that the hydrocarbons are present initially in the gaseous medium.

10 26. A method according to any preceding claim, characterised in that the gaseous medium is the exhaust emissions from an internal combustion engine.

15 27. A reactor system for treating gaseous media, including a reactor chamber (1) including at least two electrodes (405, 406) between which there is a gas permeable reactor bed (411), and means (403, 404, 407, 408, 413) for constraining the gaseous emissions to pass through the reactor bed (411), characterised in that the
20 reactor bed (411) includes a first material adapted to facilitate the establishment of an electric discharge in the interstices of the material of the reactor bed (411) and to have oxidative properties in the presence of a plasma, and a second material (412) adapted in the
25 presence of plasma activated hydrocarbon to have a catalytic action in the reduction of any nitrogenous oxides included in the gaseous medium passing through the reactor bed (411).

30 28. A reactor system according to claim 27, characterised in that the first and second materials are intimately associated in the reactor bed (411, 412) and that the ratios of the surface areas of the first and second materials (411, 412) lies in the range twenty to
35 eighty per cent.

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29. A reactor system according to claim 28,
characterised in that the reactor bed is made of a
mixture of pellets of the first and second materials
(411, 412).

5

30. A reactor system according to claim 27 or 28,
characterised in that the reactor bed 33 is divided into
two regions by a gas permeable separator 32, the upstream
region of the reactor bed consisting at least
10 predominantly of the first material.

31. A reactor system according to any of claims 27 to
30, characterised in that the first material is a
ferroelectric material.

15

32. A reactor system according to claim 31,
characterised in that the first material is barium
titanate or calcium titanate.

20 33. A reactor system according to any of claims 27 to
32, characterised in that the second material is selected
from the group comprising the aluminas known as Alcoa LD-
350, Cotal Industries CT-530, Condea hollow extrudates,
T-60 Alumina, Coriderite, α , γ and χ aluminas, mixtures of
25 the phases of alumina; zeolites; zeolites containing
iron, copper or cobalt with or without catalyst promoting
cations of cerium or lanthanum; and oxides of
cerium, titanium, vanadium and zirconium.

30 34. A reactor system according to any of claims 27 to
33, characterised in that the second material is
photocatalytic.

35 35. A reactor system according claim 34, characterised
35 in that the second material is titanium dioxide or cerium
dioxide.

36. A reactor system according to claim 35, characterised in that the second material is titanium dioxide in the anatase phase.

5

37. A reactor system according to claim 36, characterised in that the second material is titanium dioxide in the rutile phase.

10 38. A reactor system according to claim 32, characterised in that the second material is a mixture of anatase and rutile phase titanium dioxide.

15 39. A reactor system according to claim 33, characterised in that the second material is zirconia.

20 40. A reactor system according to claim 33, characterised in that the second material is a mixture of equal parts by volume of anatase phase titania and zirconia.

41. A reactor system according to any of claims 27 to 40, characterised in that the second material is a zeolite.

25

42. A reactor system according to claim 41, characterised in that the zeolite is that known as H-ZSM-5, with or without a catalytically active metal dopant.

30 43. A reactor system according to claim 41, characterised in that the zeolite is that known as mordenite with or without a catalytically active metal dopant.

35 44. A reactor system for the treatment of a gaseous medium including nitrogenous oxides characterised in that .t

- 35 -

there is provided a source (801) of a gaseous hydrocarbon, a reactor (802) to which the source of the gaseous hydrocarbon is connected, the reactor (802) containing a gas permeable bed of a material adapted to 5 have surface oxidative properties in the presence of a plasma, a second reactor (805) including a medium adapted in the presence of plasma activated hydrocarbon to catalyse the reduction of nitrogenous oxides to nitrogen, and means (803) for combining plasma activated 10 hydrocarbon from the reactor (802) with the gaseous medium prior to the combination passing into the reactor (805).

45. A reactor system according to claim 44, 15 characterised in that material in the reactor (802) is a ferroelectric material.

46. A reactor system according to claim 45, characterised in that the material is barium titanate or 20 calcium titanate.

47. A reactor system according to claims 44, 45 or claim 25 46, characterised in that the reactor (805) contains a zeolite.

48. A reactor system according to claim 47, characterised in that the zeolite is that known as H-ZSM-5, with or without a catalytically active dopant.

30 49. A reactor system according to claim 47 characterised in that the zeolite is that known as mordenite, with or without a chemical dopant.

50. A method of treating gaseous emissions including 35 carbonaceous particulates and noxious gases, including the operation of passing the gaseous emissions through a

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gas permeable reactor bed and applying across the reactor bed a potential difference sufficient to cause an electric discharge in the gaseous emissions in the interstices in the material of the reactor bed,

5 characterised in that the reactor bed includes a first material adapted to facilitate the creation of the electric discharge and a second material which in the presence of the electric discharge has a catalytic action in the reduction of nitrogenous oxides contained in the

10 gaseous emissions.

51. A method according to claim 50, characterised in that the first material is adapted also to promote the oxidation of the carbonaceous particulates contained in

15 the gaseous emissions.

52. A method according to claim 50 or claim 51, characterised in that the first and second materials are intimately associated and in that the ratio of the

20 surface areas of the first and second materials lies in the range twenty to eighty percent.

53. A method according to claim 52, characterised in that the reactor bed consists of a mixture of pellets of

25 the first and second materials.

Fig.1.

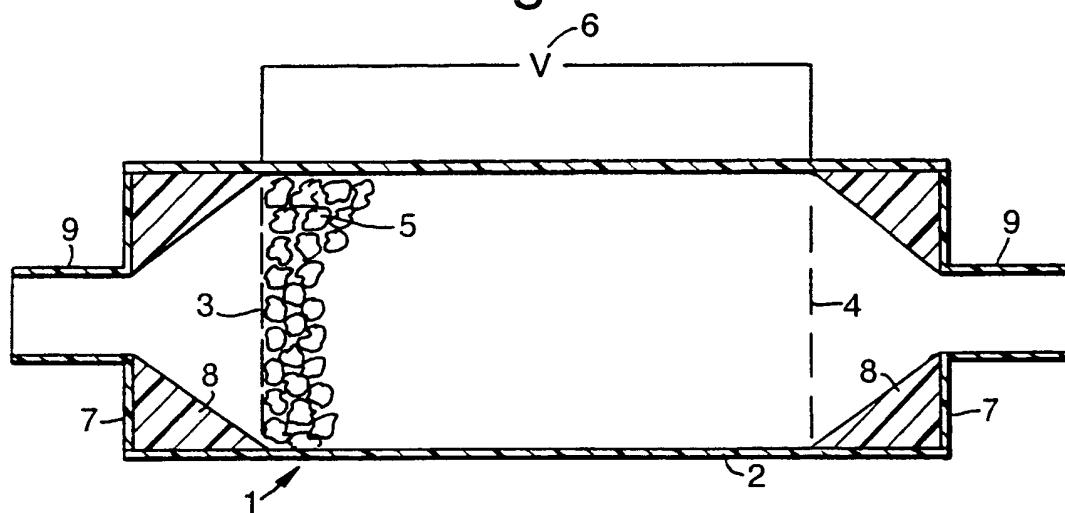


Fig.3.

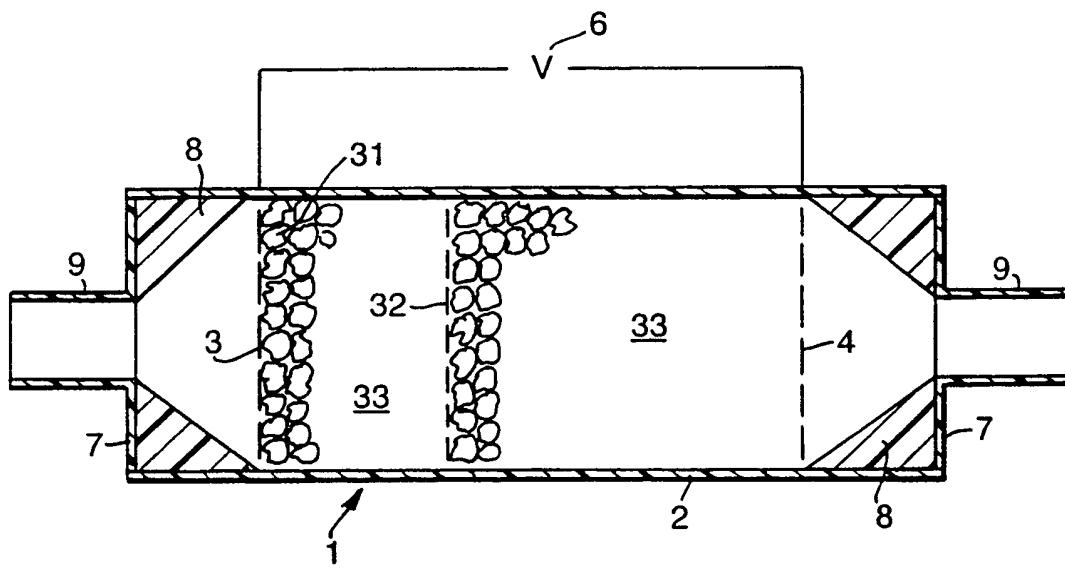


Fig.2a.

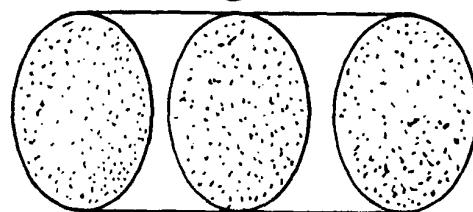


Fig.2b.

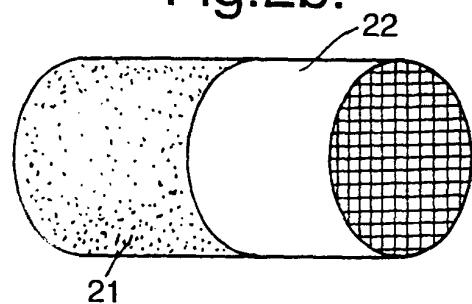


Fig.2c.

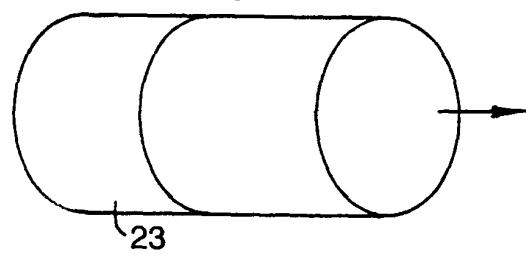


Fig.4.

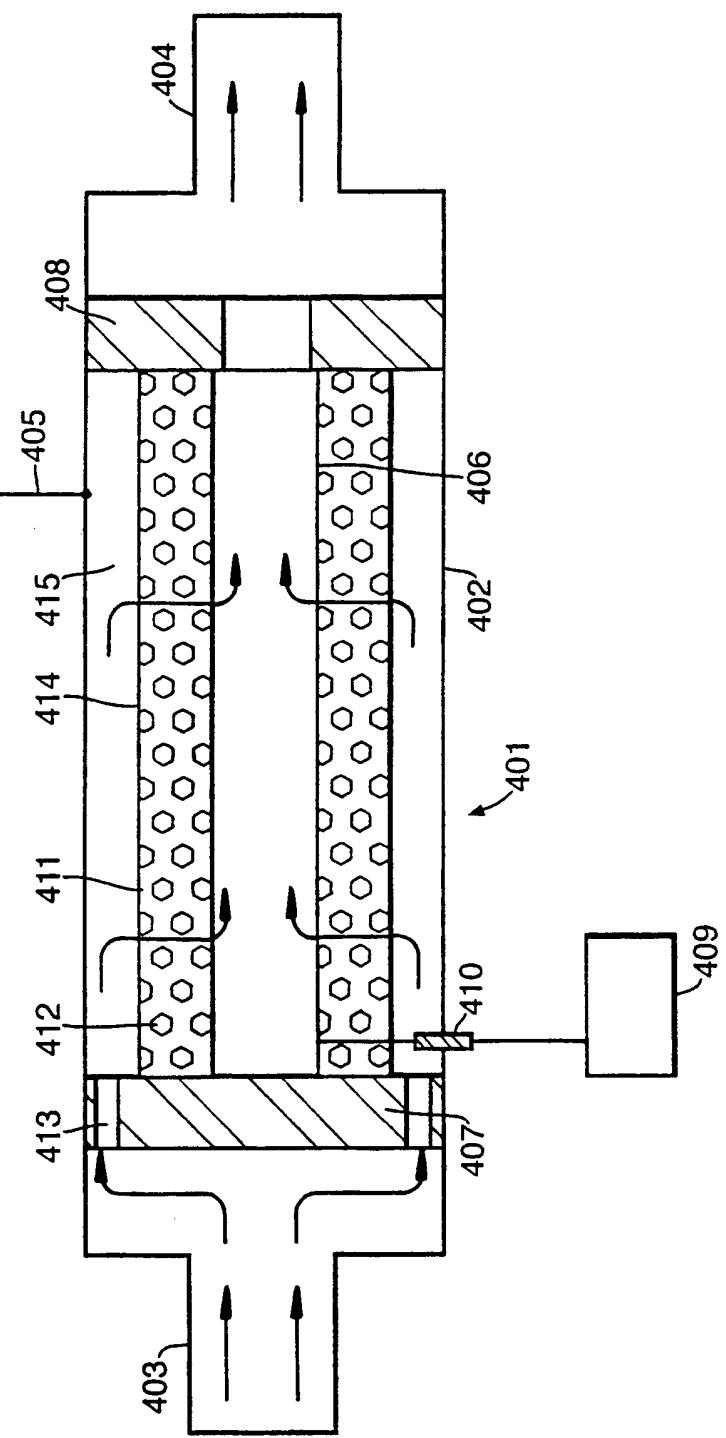


Fig.5.

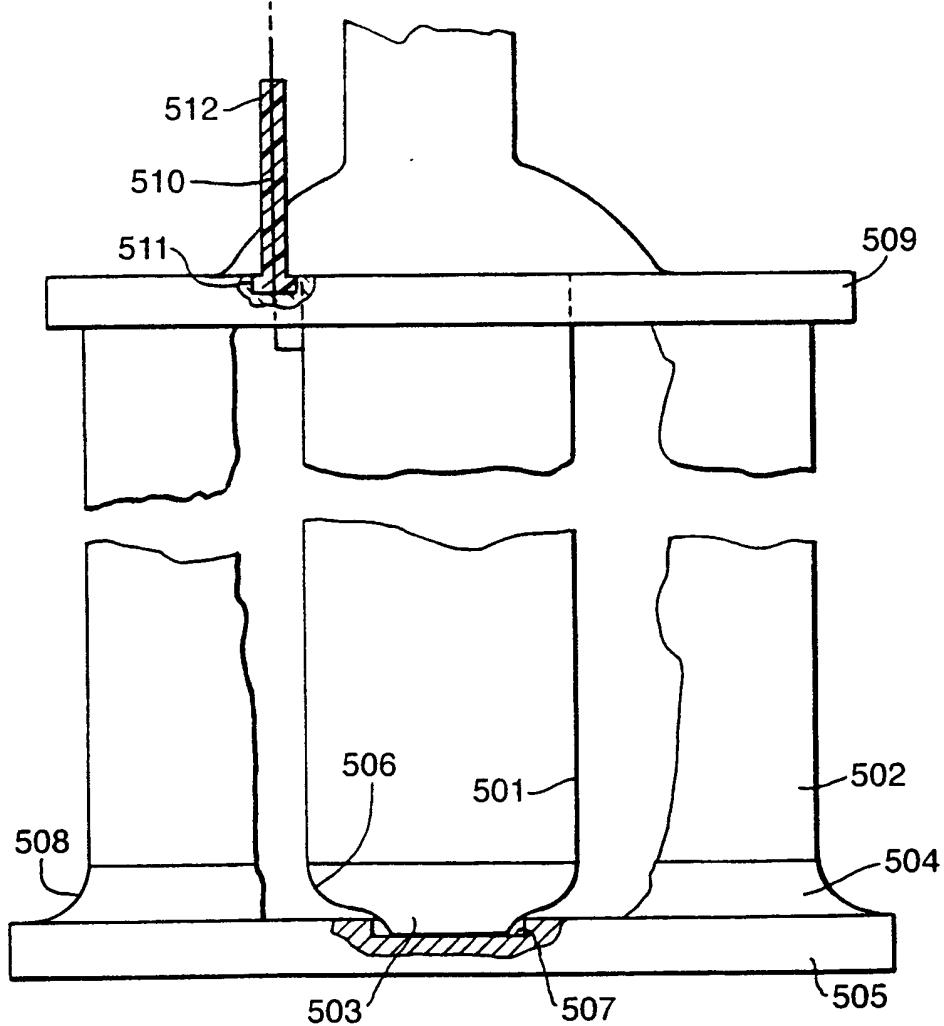


Fig.6.

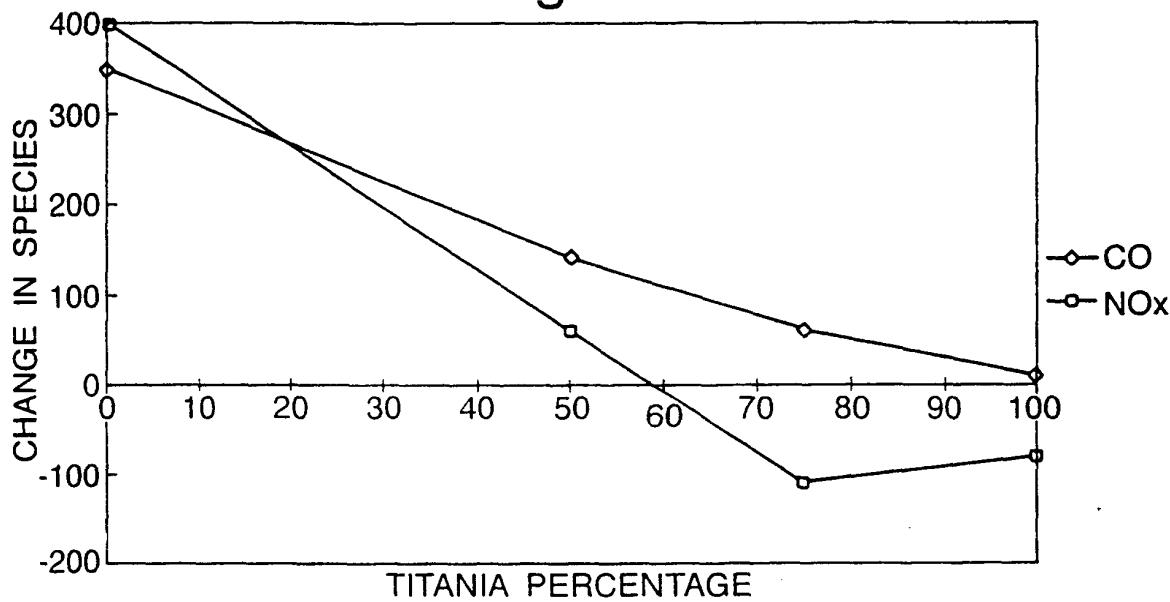


Fig.7.

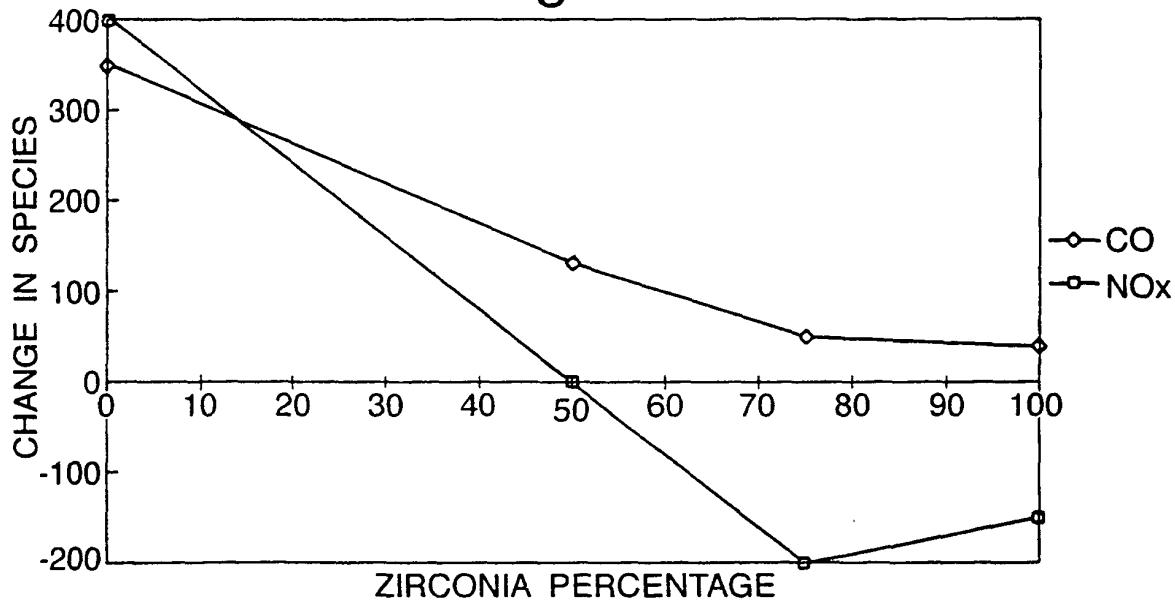


Fig.8(a).

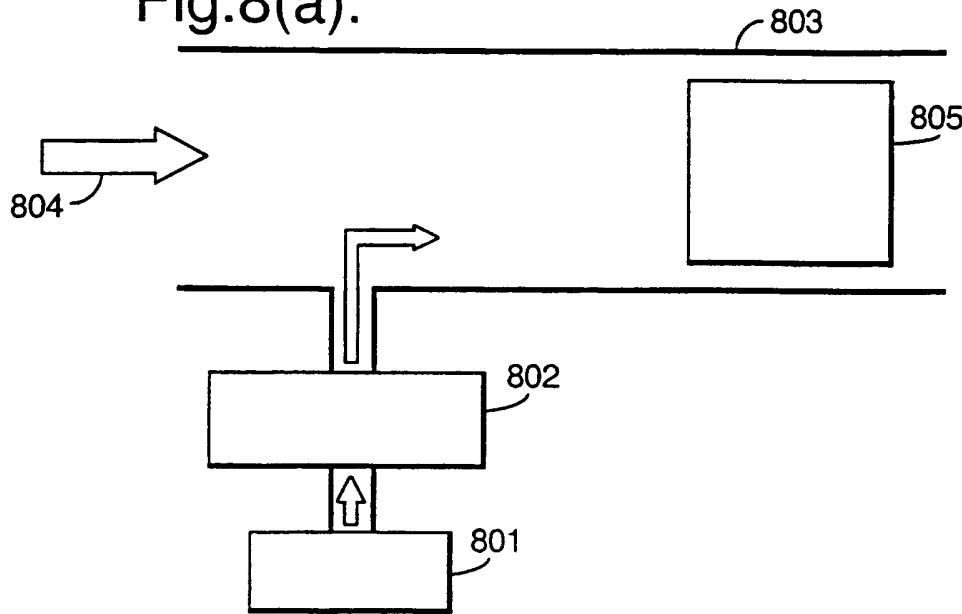


Fig.8(b).

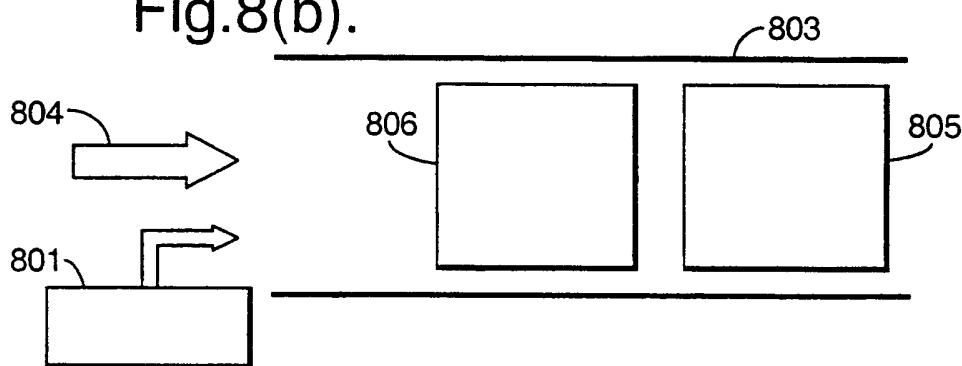
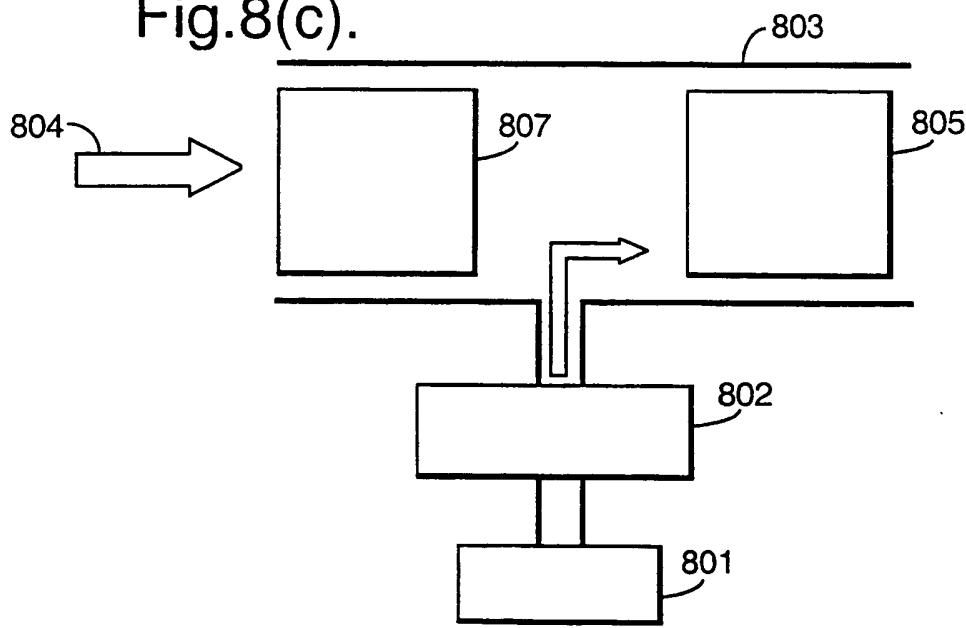


Fig.8(c).



INTERNATIONAL SEARCH REPORT

! Application No
PCT/GB 98/02569

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B01D53/32 B01D53/94 F01N3/08 B01J19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 B01D F01N B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DE 195 10 804 A (DORNIER GMBH) 26 September 1996</p> <p>see column 3, line 11 - column 5, line 1; claims 1-20; figure 1</p> <p>---</p> <p>-/-</p>	<p>1,3-7, 10-13, 16,17, 25-27, 33-36, 39,44, 45,50</p>

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/02569

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 983 021 A (HENIS JAY M) 28 September 1976 cited in the application see column 1, line 49 - column 2, line 10 see column 5, line 17 - column 6, line 27 see column 10, line 12 - line 44 see column 17, line 59 - column 18, line 69; claims 1-26; figure ---	1, 3-7, 10-13, 16, 17, 25-27, 33-36, 39, 44, 45, 50
A	GB 2 274 412 A (ATOMIC ENERGY AUTHORITY UK) 27 July 1994 cited in the application see page 1, line 3 - page 4, line 13; claims 1-23 ---	1, 2, 8, 9, 27, 31, 32, 44-46, 50, 51
A	DE 43 38 995 A (FUJITSU LTD) 1 June 1994 see column 2, line 3 - line 35 see column 4, line 53 - line 65; claims 1-39 ---	1, 3, 10-12, 16, 20, 21, 25-27, 33-35, 39, 40, 50
A	DATABASE WPI Section Ch, Week 9418 Derwent Publications Ltd., London, GB; Class E36, AN 94-147106 XP002087979 & JP 06 091138 A (MITSUI ENG & SHIPBUILDING CO), 5 April 1994 see abstract ---	1, 4, 5, 10, 19, 20, 27-29, 33, 41, 44, 47, 50, 53
A	DE 38 13 312 A (SIEMENS AG) 2 November 1989 see claims 1-23 -----	14, 15, 37, 38

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/02569

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
DE 19510804	A 26-09-1996	NONE			
US 3983021	A 28-09-1976	DE 2227949 A		04-01-1973	
		FR 2140584 A		19-01-1973	
GB 2274412	A 27-07-1994	DE 69314928 D		04-12-1997	
		DE 69314928 T		19-03-1998	
		EP 0608619 A		03-08-1994	
		JP 6241019 A		30-08-1994	
		NO 940170 A		21-07-1994	
		US 5440876 A		15-08-1995	
DE 4338995	A 01-06-1994	JP 2111722 C		21-11-1996	
		JP 6262032 A		20-09-1994	
		JP 8022367 B		06-03-1996	
		US 5474747 A		12-12-1995	
DE 3813312	A 02-11-1989	NONE			

